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Transport properties of Polyaniline -V_2O_5 Composites

Vijaykumar B. Chanashetty[1], Sharanappa.G[2*], B. M. Patil[3], Sangshetty K.[4]

[1,3]Department of Mechanical Engineering, CMJ University, Shillong, Meghalaya, India
[2]Department of Mechanical Engineering, Reva Institute of Technology, Bangalore, Karnataka, India
[4]Department of Physics, Rural Engineering College, Bhalki, Bidar, Karnataka, India
vjchan2007@gmail.com, sg_reva@gmail.com, bmpatil@yahoo.com, sangshetty_2007@rediffmail.com

Abstract

Polyaniline - V_2O_5 composites at different weight percentages were synthesized by in situ polymerization method. The composites have been synthesized with various compositions (5, 10, 15, 20, and 25 wt %) of vanadium pentaoxide in polyaniline. From the Fourier transform infrared spectroscopy (FTIR) studies on polyaniline/ V_2O_5 composites, the peak at 1122 cm^{-1} is considered to be measure of the degree of electron delocalization, 1487 cm^{-1} is C=C stretching of benzonoid ring, 1558 is C=N quinonoid stretching mode of vibration. The surface morphology of these composites was studied with scanning electron micrograph (SEM). The ac conductivity has been studied in the frequency range of 50 Hz to 5 MHz and it is found that 15 wt% shows high conductivity compare to pure polyaniline and other composites. The results obtained for these composites are of scientific and technological interest.

Keywords: Polyaniline; Vanadium pentaoxide; Composites; AC conductivity, Tangent loss

1. Introduction

Intrinsically conductive polymers have aroused a great interest among the researchers due to high mobility of the charge carriers, which also can be the excellent hosts for the trapping of metals and semiconducting nanoparticles as stabilizers or surface capping agents [1-3]. Amongst conductive polymers, polyaniline (PANI) has been widely studied owing to relative ease in preparation, good environmental stability and tunable conductivity, and showed its promising applications in many technologic fields, such as sensors, electromagnetic interference shielding, electrostatic discharge, conducting materials and corrosion inhibitors, etc [4-7]. Incorporation of inorganic compounds into PANI polymers will facilitate the combination of different features of inorganic and organic species, and the inorganic fillers in the nano-form are expected to modify the properties of the conducting polymers leading to the development of multifunctional devices [8, 9]. Among the modified properties, the enhanced conductivity was displayed due to the change in morphology of the conductive PANI in the hybrids [10, 11].

Inorganic V_2O_5 has been attracted much attention as cathodes in rechargeable ion bat-teries, selective gas sensors such as ammonia because of their high surface area and redox activity [12, 13]. One of the important aspects of the V_2O_5 is its layered lamellar structure. The layered V_2O_5 structures show intercalated nano-spaces which can be used as a reaction space of guest organic monomers [14, 15]. Monomers are incorporated into the V_2O_5 spaces and simultaneously polymerized into polymers by redox reaction with V_2O_5 layers [16, 17]. Although many studies have been conducted to form V_2O_5/polymer composite structures, controlling internal morphology has still remained a challenge.

In this paper author reports synthesis, characterization and ac conductivity of polyaniline / V_2O_5 composites of different weight percentages at room temperature. The FTIR spectra of V_2O_5 doped in polyaniline shows the characteristic peaks indicates the formation of composites. SEM image shows that the change in morphology helps in transport properties of these composites. Among all 15 wt% shows high conductivity and low dielectric constant.

2. Materials and Method

All Chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled

prior to use. Ammonium persulphate (APS) ($(NH_4)_2S_2O_8$), Hydrochloric acid (HCl), and Vanadium pentaoxide (V_2O_5) were procured from sigma and were used as received.

2.1 Synthesis of Polyaniline

The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammonium peroxydisulphate at room temperature, followed by the separation of polyaniline hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equi molar volumes of aniline and hydrochloric acid) was dissolved in distilled water in a volumetric flask to 100 mL of solution. Ammonium peroxydisulfate (0.25M) was dissolved in water also to 100 mL of solution. Both solutions were kept for 1 hour at room temperature (25°C), then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 300-mL portions of 0.2 M HCl, and similarly with acetone. Polyaniline (emeraldine) hydrochloride powder was dried in air and then in vacuum at 60°C to achieve the constant weight.

2.2 Synthesis of Polyaniline / V_2O_5 composites

0.1 mole aniline monomer is dissolved in 1 mole nitric acid to form polyaniline hydronitride. Fine graded pre-sintered V_2O_5 (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 5, 10, 15, 20 and 25 is added to the polymerization mixture with vigorous stirring in order to keep the V_2O_5 powder suspended in the solution. To this reaction mixture, APS as an oxidant is added slowly with continuous stirring for the period of 4 hrs at temperature 5^0C. Polymerization of aniline takes place over fine grade vanadium pentaoxide particles. The resulting precipitate is filtered and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any uncreated aniline. After washing, the precipitate is dried under dynamic vacuum at 60^0C for 24 h to achieve constant weight of resulting composites [18]. In this way five different polyaniline / V_2O_5 composites with different weight percentage of vanadium pentaoxide (5, 10, 15, 20 and 25) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium.

2.3 Preparation of Pellets

The powders of polyaniline and polyaniline – V_2O_5 composites so obtained from synthesis techniques discussed in the early sections are crushed and finely in the presence of acetone medium in agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness which varies from 1 to 2 mm by applying pressure of 90 MPa in a hydraulic press. The pellets of polyaniline and its composites so obtained from above mentioned techniques are coated with silver paste on either side of the surfaces to obtain better contacts.

3. Characterization

The FTIR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording FTIR spectra, powders are mixed with KBr in the ratio 1:25 by weight to ensure uniform dispersion in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of approximately 1 mm thickness. The morphology of the composites in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope. The Dielectric tangent loss and dielectric constant are studied by sandwiching the pellets of these composites between the silver electrodes and is studied in the frequencies 10^2Hz – 10^6Hz, using Hioki LCR Q meter.

3.1 FTIR Spectroscopy of polyaniline and its composites

Figure 1(a) shows FTIR spectra of pure polyaniline. The characteristic vibration of polyaniline is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of PANI shows vibrations around 499, 592, 617, 814, 1024, 1122, 1240,1300, 1487, 1556, 2860, 2924, 3447cm^{-1}. The band at 499 is stretching out of plane, 592 corresponds to aromatic ring, 617 is for metal oxygen stretching, 814 is plane bonding of C-H bonding aromatic ring, 1024 is S-O vibration, 1122 is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1303 is C-N aromatic

amines, 1487 is C=C stretching of benzonoid ring, 2860 and 2924 are C-H stretching, 3447 is N-H stretching vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline [19].

Figure 1(b) shows FTIR spectra of 5 wt% of polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline/V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 509, 580, 698, 808, 879, 1140, 1238, 1304, 1485, 1558, 2922cm^{-1}. The band at 509, 580, 698 are metal oxygen stretching, 808 corresponds to plane bonding of C-H bond aromatic ring, 879 is C-H bond, 1140 is C-O-C stretching excess oxidant, 1238 is C-N stretching of benzonoid ring, 1304 is C-N aromatic amines, 1485 is C=C stretching of benzonoid ring, 1558 is C=N quinonoid stretching mode of vibration, 2922 is C-H stretching. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite.

Figure 1(c) shows FTIR spectra of 10 wt% polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline /V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 507, 582, 702, 804, 877, 1141, 1242, 1304, 1485, 1556cm^{-1}. The band at 507, 582, 702 are metal oxygen stretching, 804 corresponds to plane bonding of C-H bond aromatic ring, 877 is C-H bond, 1141 is C-O-C stretching excess oxidant, 1242 is C-N stretching of benzonoid ring, 1304 C-N aromatic amines, 1485 C=C is stretching of benzonoid ring , 1556 is C=N quinonoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite.

Figure 1(d) shows FTIR spectra of 15 wt% polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline /V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 507, 594, 700, 804, 871, 1140, 1240, 1304, 1475, 1558cm^{-1}. The band at 507, 594, 700 are metal oxygen stretching, 804 corresponds to plane bonding of C-H bond aromatic ring, 871 is C-H bond, 1140 is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1304 is C-N aromatic amines, 1475 is C=C stretching of benzonoid ring , 1558 is C=N quinonoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite.

Figure 1(e) shows FTIR spectra of 20 wt% of polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline /V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 408, 511, 580, 700, 802, 877, 1143, 1236, 1304, 1481, 1558cm^{-1}. The band at 408 is out of plane, 511, 580, 700 are metal oxygen stretching, 802 corresponds to plane bonding of C-H bond aromatic ring, 877is C-H bond, 1143 is C-O-C stretching excess oxidant, 1236 is C-N stretching of benzonoid ring, 1304 is C-N aromatic amines, 1481 is C=C stretching of benzonoid ring, 1558 is C=N quinonoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite.

Figure 1(f) shows FTIR spectra of 25 wt% polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline /V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 507, 590, 704, 806, 875, 1134, 1240, 1304, 1479, 1556cm^{-1}. The band at 507, 590, 704 are metal oxygen stretching, 806 corresponds to plane bonding of C-H bond aromatic ring, 875 is C-H bond, 1134 is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1304 is C-N aromatic amines, 1479 is C=C stretching of benzonoid ring , 1556 is C=N quinonoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite [20].

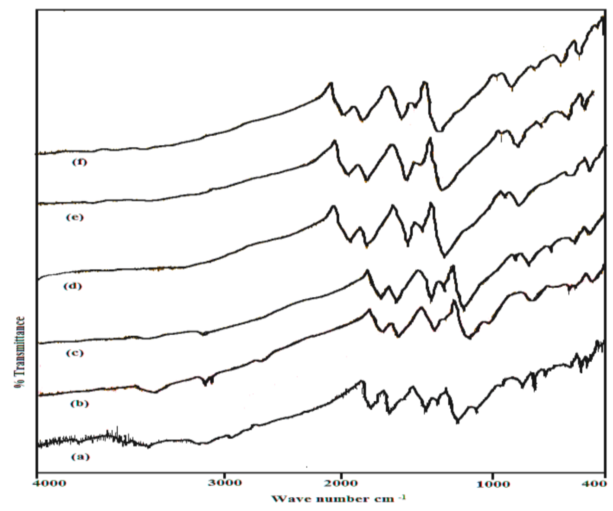


Figure 1(a-f): shows the FTIR spectra of PANI/V_2O_5 composites of different weight percentage.

3.2 Scanning Electron Microscopy (SEM)

Figure 2(a) shows that Scanning Electronic Micrograph (SEM) image of pure polyaniline. Highly agglomerated granular in shape and has amorphous nature. The average grain size was found to be 2 to 4µm. The grains are well interconnected with each other which indicate that they have enough binding energy to combine with neighbor grains or molecules.

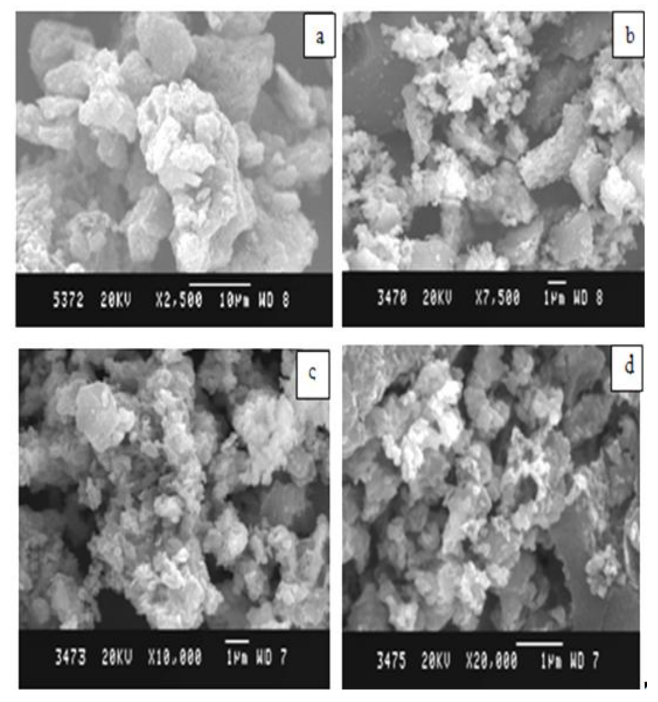


Figure 2 (a-d): show the SEM image of PANI and PANI/V_2O_5 composites of different weight percentage (5, 15 and 25 wt %)

The SEM image of 5 wt % of PANI/ V_2O_5 composites shown in figure 2(b). The grains are highly agglomerated, irregular in shape but they are well interconnected each others. The average grain size was found to be 0.22µm. The SEM image of 15 wt % of PANI/ V_2O_5 composites shown in figure 2(c). It is observed from the image that all grains are irregular in structure arranged one above the others. The average grain size was found to be 0.43µm. Figure 2(d) shows the SEM image of 25 wt % of PANI/V_2O_5 composites prepared at room temperature. It is found that from the image the grains are high agglomerated, have porosity and good interconnectivity between the particles. The average grain size was found to be 0.53µm.

By comparing the figure (a-d), it can be conclude that the gradual increase in granular size and change in morphology helps the transportation of charge particles through the carbon back-bone of polymer chains [21].

3.3 Ac Conductivity

3.3.1 Polyaniline – V_2O_5 composites

Figure 3 shows the variation of ac conductivity as a function of frequency for Polyaniline – V_2O_5 composites (different wt %). It is observed that in all the cases, σ_{ac} remains constant up to 10^5 Hz. Among all composites, 15 wt% of polyaniline / V_2O_5 composites shows high conductivity due to interfacial polarization. However, in case of polyaniline and other composites 5, 10, 20 and 25 wt% the conductivity value is low because of dipole polarization. This behavior of these composites may be due to the variation in the distribution of V_2O_5 particles in polyaniline.

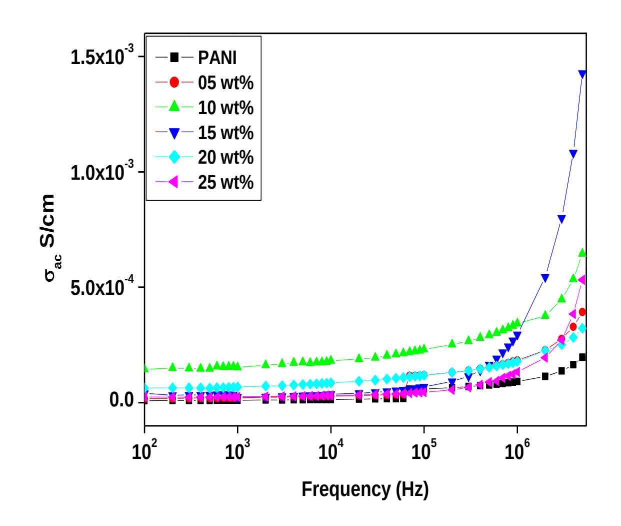


Figure 3: shows the variation of □$_{ac}$ conductivity as a function of frequency for polyaniline – V_2O_5 composites (different wt %).

Figure 4 shows the variation of ε' as a function of frequency for Polyaniline – V_2O_5 composites (different wt %). In all the cases it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency. The observed behavior may be due to Debye like relaxation mechanism taking place in these materials. Among all 25 wt% of PANI - V_2O_5 composites shows high permittivity due to relaxation mechanism and may be also as it exceeds critical contraction [22].

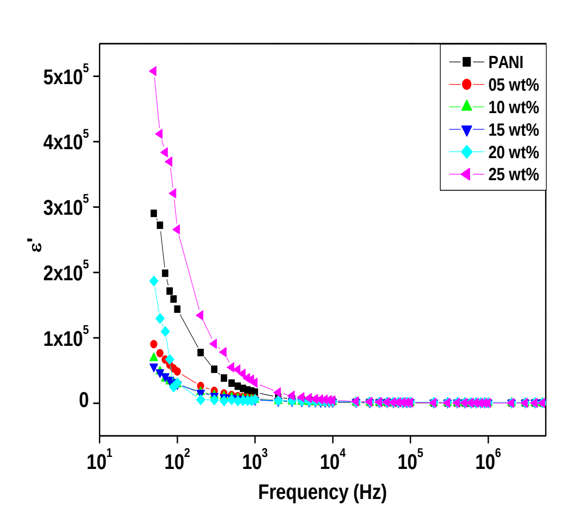


Figure 4: shows the real part permittivity as a function of frequency of PANI- V_2O_5 composites at different weight percentage

The variation of dielectric loss as a function of frequency for Polyaniline – V_2O_5 composites (different wt %) is represented in figure 5. Even though V_2O_5 is added up to 25 wt% in polyaniline, the behavior of dielectric loss with respect to frequency follows the same trend as that of pure polyaniline. At higher frequencies these composites exhibit almost zero dielectric loss which suggests that these composites are lossless materials at frequencies beyond 1 MHz [23].

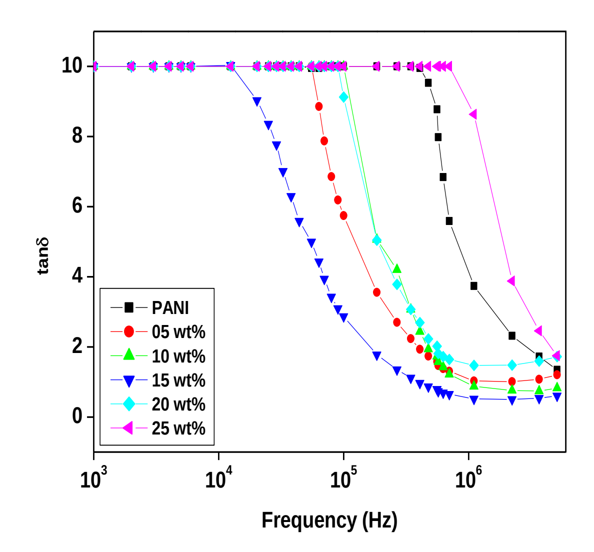


Figure 5: shows the variation of tan as a function of frequency of PANI- V_2O_5 composites at different weight percentage

4. Conclusion

The inorganic V_2O_5 doped polyaniline composites has been prepared at different weight percentages (5, 10, 15, 20, and 25 wt %) were synthesized by in situ polymerization method. From the Fourier transform infrared spectroscopy (FTIR) studies on polyaniline/ V_2O_5 composites, the peak at 1122 cm^{-1} is considered to be measure of the degree of electron delocalization, 1487 cm^{-1} is C=C stretching of benzonoid ring, 1558 is C=N quinonoid stretching mode of vibration. This confirms the formation of polyaniline/V2O5 composites. The surface morphology of these composites was studied with scanning electron micrograph (SEM) and it is observed that 15 wt% of composites have well interconnectivity of grains, which is favourable for transport of charge carriers. The ac conductivity has been studied in the frequency range of 50 Hz to 5 MHz and shows 15 wt% high conductivity of 1.4x10^{-3} S/cm as well as low dielectric constant compare to pure polyaniline and other composites.

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